WADD TECHNICAL REPORT 60-782
PART II

VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE

Part II. Mass Spectrometric Studies of the Vaporization of Sulphides and the Dissociation Energy of S_2

R. Colin
P. Goldfinger
M. Jeunehomme

University of Brussels
Brussels, Belgium

NOVEMBER 1960

WRIGHT AIR DEVELOPMENT DIVISION

WADD TECHNICAL REPORT 60-782
PART II

VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE

Part II. Mass Spectrometric Studies of the Vaporization of Sulphides and the Dissociation Energy of S_2

R. Colin
P. Goldfinger
M. Jeunehomme

University of Brussels
Brussels, Belgium

NOVEMBER 1960

Materials Central
Contract No. AF 61(052)-225
Project No. 7350

WRIGHT AIR DEVELOPMENT DIVISION
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

600 – May 1961 – 29-1115

FOREWORD

This report was prepared by the University of Brussels, Belgium, under USAF Contract No. AF 61(052)-225. The contract was initiated under Project No. 7350, "Refractory Inorganic Nonmetallic Materials, " Task No. 73500, "Ceramic and Cermet Materials Development". The work was administered under the directorate of Advanced Systems Technology, Wright Air Development Division, with Mr. F. W. Vahldiek acting as project engineer.

This report covers work conducted from March 1959 through March 1960.

The authors wish to thank the Comite Belge de Spectrometrie de Masse (I.R.S.I.A.) which made available part of the equipment used in this report.

ABSTRACT

The equilibria $S_2 \rightleftharpoons 2S$ and $CaS \rightleftharpoons Ca + S$ have been observed in the vapor phase above CaS. $D_o^o(S_2) = 4.4 \pm 0.2$ e.v., $D_o^o(SO) = 5.4 \pm 0.2$ e.v., $D_o^o(CaS) = 3.7 \pm 0.2$ e.v., and $\Delta H_{298}^{vap}(CaS) = 5.9 \pm 0.2$ e.v. have been determined mass spectrometrically.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

W. C. RAMKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Laboratory
Materials Central

TABLE OF CONTENTS

MASS SPECTROMETRIC STUDIES OF THE VAPORIZATION OF SULPHIDES AND THE DISSOCIATION ENERGY OF S_2.

DISCUSSION

The disagreement between second and third law values of the dissociation energy of S_2 ($D_c^\circ(S_2)$) obtained from equilibrium measurements has been emphasized many years ago[1]. A relationship was also pointed out between the heat of combustion of SO, $D_o^\circ(O_2)$, $D_o^\circ(SO)$, and $D_o^\circ(S_2)$, which should permit one to choose one of the values allowed by observed predissociations for $D_o^\circ(S_2)$ and $D_o^\circ(SO)$. Recent measurements[2] do not seem to settle the question[3].

In the vapour phase above CaS we have observed by mass spectrometry[4] the dissociation $S_2 \rightleftharpoons 2S$, and $CaS \rightleftharpoons Ca + S$ and have calculated $D_o^\circ(S_2) = 4.4 \pm 0.2$ e.v., $D_o^\circ(SO) = 5.4 \pm 0.2$ e.v. $D_o^\circ(CaS) = 3,7 \pm 0.2$ e.v. and $\Delta H_{298}^{vap}(CaS) = 5.9 \pm 0,2$ e.v.

Manuscript released for publication 26 March 1960 as a WADD Technical Report.

The mass spectrometric method has been described previously [4,5]. The sample was heated in a molybdenum Knudsen cell ; provisions were made to distinguish between residual gas molecules and those of the beam which passes through a cooled collimation system ; ion intensities were measured with an electron multiplier. Absolute values of partial vapour pressures were obtained from $P_i = I_i T/S_i$; I_i is the measured current corresponding to a species i, T the absolute temperature of the Knudsen cell, and S_i the sensitivity for i :

(6) $S_i = (M_i/2\pi R)^{1/2}(s/G_i) \sum I_i T^{1/2} \Delta t$; M_i is its molecular mass, R the gas constant, s the area of the effusion orifice and t the time necessary to evaporate the weight G_i of species i .

Brightness temperatures of a small threaded hole at the bottom of the Knudsen cell have been measured with an optical pyrometer; emissivity and window corrections were made. [7]

Dissociation energies were calculated from: $D^{\circ}_{o} = - RT\ln K + T\Delta((F^{\circ}_{T} - H^{\circ}_{o})/T)$ (3d law) and : $D^{\circ}_{T} = R d\ln K/d(1/T)$ (2d law) using free energy functions taken from Stull and Sinke[8], or for CaS, calculated by comparison of oxides and sulphides, assuming ω_e = 390 cm^{-1}, r_e = 2.3 A and that only the $^1\Sigma$ ground state is important.

Ionization cross sections were taken from Otvos and Stevenson[9] and it was assumed that those of molecules are equal to the sum of those of the constituent atoms. The mass effect and the molecular effect of the multiplier[10] were considered to compensate each other. A possible error of 20° in the temperature measurement would lead to an uncertainty of 12 % in the second law and of 1% in the third law values ; instead of the assumptions made above, it may be reasonable that the product of ionization cross section and multiplier gain is the same for the atom and for the molecule[11] :

in that case the 3d law D_o^o values of Table I are increased by about + 3.5 kcal. and $\Delta H_{298}^{vap}(CaS)$ diminished by the same amount.

The data of Table I and $\Delta H_{298}^{vap}(Ca)$ [8] = 42.2 kcal. ΔH_{298}^{o} (1/2 S_2) = 15.4 kcal, the standard heat of formation ΔH_{298}^{o} f.(CaS) = 110.0 ± 2 kcal [12] permit one to calculate $\Delta H_{298}^{vap}(CaS)$ = 136 kcal. The value obtained from this cycle is considered as more reliable than that given in table I (see remark table I).

$D_o^o(S_2)$ obtained here, combined with $\Delta H_o^o(SO)$ [2b] for the reaction 1/2 S_2 + 1/2 $O_2 \rightleftharpoons$ SO definitely rules out a value $D_o^o(SO)$ smaller than 5.2 e.v. There are good spectroscopic arguments for $D_o^o(SO)$ = 5.358 e.v. [13] rather than 5.027 e.v. [3]. Our measurements are not accurate enough to permit one to settle the question whether the predissociation at 4.41 e.v. gives the exact dissociation of S_2 [14] or an upper limit [15]; a value $D(S_2)$ = 4.2 e.v. would agree with our results [16]. Within the accuracy quoted in Table I, all available data

on $D(S_2)$ and $D(SO)$[3] except appearance potential measurements [17] and older equilibrium measurements (cf. 1,2,3,14) seem to be in agreement.

REFERENCES

(1) P.Goldfinger, W.Jeunehomme and B.Rosen, Nature, 138, 205 (1936).

(2) a) G.St. Pierre and J.Chipman, J.Am.Soc., 76, 4787 (1954) ; J.Metals, 8, 1474 (1956) ;
b) E.W.Dewing and F.D.Richardson, Trans. Faraday Soc., 54, 679 (1958).

(3) a) L.Brewer, J.Chem.Phys., 31, 1143 (1959) ;
b) D.G.H. Marsden, ibid., 1143.

(4) P.Goldfinger and M.Jeunehomme "Advances in Mass Spectrometry", (Pergamon Press, London, 1959) p.534.

(5) J.Drowart and P.Goldfinger, J.Chem.Phys., 55, 721 (1958).

(6) P.Goldfinger, M.Ackerman and M.Jeunehomme, Final Technical Report, EOARDC, contract N° AF 61(052)-19 (1959) ; R.Colin P.Goldfinger, M.Jeunehomme and G.Verhaegen, A.C.S. National Meeting, Atlantic City, Sept. 13-18 1959. (to be published).

(7) M.Ackerman, F.Stafford and J.Drowart (to be published).

(8) D.R.Stull and G.C.Sinke, "Thermodynamic Properties of the Elements", American Chemical Society, November 1956.

(9) J.W.Otvos and D.P.Stevenson, J.Am.Chem.Soc., 78, 546 (1956).

(10) M.G.Inghram and R.J.Hayden, Nuclear Science Series, Report N° 14, National Research Council, Washington, D.C.1954; M.G.Inghram, R.J.Hayden and D.C. Hess in N.B.S. Circ. 522 Washington (1953) p.257; H.E. Stanton, W.A. Chupka, M.G.Inghram. Rev.Sci.Instr., 27, 109 (1956).

(11) P.Schissel, J.Chem.Phys., 26, 1276 (1957).

(12) O.Kubatschewski and E.Ll. Evans, "Metallurgical Thermochemistry", Pergamon Press Ltd., London (1956).

(13) R.G.W. Norrish and G.A.O. Oldershaw, Proc. Roy.Soc. (London) A. 249 498 (1959).

(14) A.G.Gaydon,"Dissociation Energies," second edition. Chapman and Hall Ltd. (London) (1953).

(15) G.Herzberg and L.G.Mundie, J.Chem.Phys., 8, 263 (1940).

(16) A.D.Walsh in "Threshold of Space", in Proc.Conf. on Chemical Aeronomy in Cambridge, Mass. 1956, M.Zelikoff editor (Pergamon Press, N.Y., 1957).

(17) L.P.Blanchard and P.Le Goff, Can.J.Chem., 35, 89 (1957) ; V.H.Dibeler, J.L.Franklin and R.M. Reese, J.Chem.Phys., 29 880 (1958).

Table I. Heats of Vaporization and Dissociation Energies of S_2 and CaS

T°K	logp(S)*	logp(S_2)	logp(Ca)	logp(CaS)	$D^o_o(S_2)$ kcal	D^o_o(Cas) kcal	H^{vap}_{298}(CaS) kcal
1922	-5.96	-6.56	-6.15	-	100	-	-
1975	-5.46	-6.25	-5.79	-	96.5	-	-
2026	-5.34	-6.01	-5.54	-	98.0	-	-
2048	-5.04	-5.82	-5.35	-	96.4	-	-
2053	-5.03	-5.83	-5.32	-7.26	96.4	79.8	151.9
2070	-5.18	-5.88	-5.42	-7.03	98.8	84.9	149.0
2098	-4.86	-5.63	-5.13	-6.99	97.3	80.7	151.5
2143	-4.76	-5.48	-5.03	-6.66	98.9	83.7	151.6
2144	-4.60	-5.38	-4.90	-6.72	96.7	80.3	152.2
2154	-4.71	-5.44	-4.99	-	98.8	-	-
2156	-4.64	-5.38	-4.86	-6.71	96.8	80.1	152.9
2190	-4.52	-5.28	-4.75	-6.55	98.3	81.5	153.6
2223	-4.27	-5.02	-4.58	-6.27	97.4	81.3	153.7
2297	-3.98	-4.82	-4.24	-5.99	96.8	80.3	155.6
				average	97.6	81.4	152.4**
				slope method	108	95	129
			proposed values		101 ± 5	86 ± 5	136 ± 10

* Decimal logarithms of pressures in atmospheres.

** $F^o_T - H^o_{298}/T$ for this process in based on very scanty data on C_p (CaS) (K. K. Kelley, U.S. Bureau of Mines Bulletin 476, Washington D. C. , 1949)

UNCLASSIFIED

UNIVERSITY OF BRUSSELS, Brussels, Belgium
VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE. Part II Mass Spectrometric Studies of the Vaporization of Sulphides and the Dissociation Energy of S_2, by R. Colin, P. Goldfinger and M. Jeunehomme. November 1960 8pp. table. (Project No. 7350; Task 73500)(ASD TR 60-782 Pt II)(Contract No. AF 61(052)-225.
Unclassified report

The equilibria $S_2 \rightleftharpoons 2S$ and $CaS \rightleftharpoons Ca+S$ have been observed in the vapor phase above CaS. $D^{\circ}_0(S_2)=4.4\pm0.2$ e.v., $D^{\circ}_0(SO)=5.4\pm0.2$ e.v., $D^{\circ}_0(CaS)=3.7\pm0.2$ e.v. and $\Delta H^{298}_{298}(CaS)=5.9\pm$ 0.2 e.v. have been determined.

(over)

UNCLASSIFIED

UNIVERSITY OF BRUSSELS, Brussels, Belgium
VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE. Part II Mass Spectrometric Studies of the Vaporization of Sulphides and the Dissociation Energy of S_2, by R. Colin, P. Goldfinger and M. Jeunehomme. November 1960 8pp. table. (Project No. 7350; Task 73500)(ASD TR 60-782 Pt II)(Contract No. AF 61(052)-225.
Unclassified report

The equilibria $S_2 \rightleftharpoons 2S$ and $CaS \rightleftharpoons Ca+S$ have been observed in the vapor phase above CaS. $D^{\circ}_0(S_2)=4.4\pm0.2$ e.v., $D^{\circ}_0(SO)=5.4\pm0.2$ e.v., $D^{\circ}_0(CaS)=3.7\pm0.2$ e.v. and $\Delta H^{298}_{298}(CaS)=5.9\pm$ 0.2 e.v. have been determined.

(over)

UNCLASSIFIED

UNCLASSIFIED

UNIVERSITY OF BRUSSELS, Brussels, Belgium
VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE. Part II Mess Spectrometric Studies of the Vaporization of Sulphides and the Dissociation Energy of S_2, by R. Colin, P. Goldfinger and M. Jeunehomme. November 1960 8pp. table. (Project No. 7350; Task 73500)(ASDD TR 60-782 Pt II)(Contract No. AF 61(052)-225.
Unclassified report

The equilibria $S_2 \rightleftharpoons 2S$ and $CaS \rightleftharpoons Ca+S$ have been observed in the vapor phase above CaS. $D^\circ_0(S_2)$=4.4±0.2 e.v., $D^\circ_0(SO)$=5.4±0.2 e.v., $D^\circ_0(CaS)$=3.7±0.2 e.v. and $\Delta H^{vap}_{298}(CaS)$=5.9± 0.2 e.v. have been determined.

(over)

UNCLASSIFIED

UNCLASSIFIED

UNIVERSITY OF BRUSSELS, Brussels, Belgium
VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE. Part II Mess Spectrometric Studies of the Vaporization of Sulphides and the Dissociation Energy of S_2, by R. Colin, P. Goldfinger and M. Jeunehomme. November 1960 8pp. table. (Project No. 7350; Task 73500)(ASDD TR 60-782 Pt II)(Contract No. AF 61(052)-225.
Unclassified report

The equilibria $S_2 \rightleftharpoons 2S$ and $CaS \rightleftharpoons Ca+S$ have been observed in the vapor phase above CaS. $D^\circ_0(S_2)$=4.4±0.2 e.v., $D^\circ_0(SO)$=5.4±0.2 e.v., $D^\circ_0(CaS)$=3.7±0.2 e.v. and $\Delta H^{vap}_{298}(CaS)$=5.9± 0.2 e.v. have been determined.

(over)

UNCLASSIFIED

UNCLASSIFIED

UNIVERSITY OF BRUSSELS, Brussels, Belgium
VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE. Part II Mass Spectrometric Studies of the Vaporization of Sulphides and the Dissociation Energy of S_2, by R. Colin, P. Goldfinger and M. Jeunehomme. November 1960 8pp. table. (Project No. 7350; Task 73500)(ASDD TR 60-782 Pt II)(Contract No. AF 61(052)-225. Unclassified report

The equilibria $S_2 \rightleftharpoons 2S$ and $CaS \rightleftharpoons Ca+S$ have been observed in the vapor phase above CaS. $D_0^\circ(S_2)=4.4\pm0.2$ e.v., $D_0^\circ(SO)=5.4\pm0.2$ e.v., $D_0^\circ(CaS)=3.7\pm0.2$ e.v. and $\Delta H_{298}^{\circ 3P}(CaS)=5.9\pm 0.2$ e.v. have been determined.

(over)

UNCLASSIFIED

UNCLASSIFIED

UNIVERSITY OF BRUSSELS, Brussels, Belgium
VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE. Part II Mass Spectrometric Studies of the Vaporization of Sulphides and the Dissociation Energy of S_2, by R. Colin, P. Goldfinger and M. Jeunehomme. November 1960 8pp. table. (Project No. 7350; Task 73500)(ASDD TR 60-782 Pt II)(Contract No. AF 61(052)-225. Unclassified report

The equilibria $S_2 \rightleftharpoons 2S$ and $CaS \rightleftharpoons Ca+S$ have been observed in the vapor phase above CaS. $D_0^\circ(S_2)=4.4\pm0.2$ e.v., $D_0^\circ(SO)=5.4\pm0.2$ e.v., $D_0^\circ(CaS)=3.7\pm0.2$ e.v. and $\Delta H_{298}^{\circ 3P}(CaS)=5.9\pm 0.2$ e.v. have been determined.

(over)

UNCLASSIFIED

UNCLASSIFIED

UNIVERSITY OF BRUSSELS, Brussels, Belgium
VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE. Part II Mass Spectrometric Studies of the Vaporization of Sulphides and the Dissociation Energy of S_2, by R. Colin, P. Goldfinger and M. Jeunehomme. November 1960 8pp. table. (Project No. 7350; Task 73500)(ASD TR 60-782 Pt II)(Contract No. AF 61(052)-225. Unclassified report

The equilibria $S_2 + 2S$ and $CaS \rightleftharpoons Ca+S$ have been observed in the vapor phase above CaS. $D^\circ_0(S_2)=4.4\pm0.2$ e.v., $D^\circ_0(SO)=5.4\pm0.2$ e.v., $D^\circ_0(CaS)=3.7\pm0.2$ e.v. and $\Delta H^{vap}_{298}(CaS)=5.9\pm0.2$ e.v. have been determined.

(over)

UNCLASSIFIED

UNCLASSIFIED

UNIVERSITY OF BRUSSELS, Brussels, Belgium
VAPORIZATION OF COMPOUNDS AND ALLOYS AT HIGH TEMPERATURE. Part II Mass Spectrometric Studies of the Vaporization of Sulphides and the Dissociation Energy of S_2, by R. Colin, P. Goldfinger and M. Jeunehomme. November 1960 8pp. table. (Project No. 7350; Task 73500)(ASD TR 60-782 Pt II)(Contract No. AF 61(052)-225. Unclassified report

The equilibria $S_2 + 2S$ and $CaS \rightleftharpoons Ca+S$ have been observed in the vapor phase above CaS. $D^\circ_0(S_2)=4.4\pm0.2$ e.v., $D^\circ_0(SO)=5.4\pm0.2$ e.v., $D^\circ_0(CaS)=3.7\pm0.2$ e.v. and $\Delta H^{vap}_{298}(CaS)=5.9\pm0.2$ e.v. have been determined.

(over)

UNCLASSIFIED